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(54) Preparation of well dispersed suspensions for spray drying

(57) A procedure for making well dispersed suspensions containing mixtures of WC and Co powders displaying a low viscosity which remain stable over an extended period of time is described. The suspensions are prepared in aqueous or ethanolic media using a cationic polyelectrolyte - polyethylenimine - at the inherent pH of the mixture. The method is particularly useful for making robust slurries for subsequent spray drying of free flowing granules to be used in the fabrication of cemented carbide bodies.

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Description

Field of the invention

[0001] This invention relates to a process of preparing robust, homogeneous, well-dispersed aqueous and ethanolic multicomponent mixtures of WC+Co (hard metal)-based materials.

Background of the invention

[0002] It is of utmost importance to be able to control all of the steps in the manufacturing of reliable products using a powder metallurgy approach. For optimum performance and high reliability, materials produced by a powder metallurgy route should have a microstructure characterised by a small defect size, other phases well dispersed and a homogeneous grain boundary composition. One of the problems limiting the development of materials with these characteristics relates to the difficulty of achieving a good mix of two or more particulate materials to obtain homogeneous composite mixtures. Since fine powders are cohesive and thus difficult to mix in the dry state, most mixing is performed in the wet state. Typically, the particulate components are mixed with a liquid, a proper dispersant and possibly further additives so that a well dispersed, non-agglomerated slurry can be made. If this is done right, i.e. a proper dispersant is used to disperse the powder, it is possible to obtain a very good homogeneous particulate mixture.

[0003] The slurry is then processed further. One of the most common shaping methods involves dry pressing; this requires the production of free flowing granules, usually by spray drying. This is the most common method of producing hard metal (WC+Co-based) inserts for metal cutting applications. It is clear that spray drying of fine powders in large quantities requires a high degree of process control to reach the desired microstructural characteristics and size distribution of the granules. One of the controlling parameters of the spray drying process is the viscosity of the slurry. It is preferred that the slurry should display a low viscosity at the appropriate shear rates. Shear thickening has to be avoided; a sudden increase in viscosity at high shear rates may cause clogging or serious damage to the spraying nozzle.

[0004] The importance of the suspensions for reliable processing has resulted in a substantial interest in developing technologies and methods for preparing well dispersed, homogeneous particulate slurries displaying a low viscosity. Well-established recipes exist today for several materials in both aqueous and non-aqueous media. A commercial dispersant, Hypermer KD3, produced by ICI Chemicals has proved to disperse a wide range of ceramic powders in non-polar media, e.g. silicon nitride (L. Bergstrom, "Rheological properties of concentrated, non-aqueous silicon nitride suspensions", J. Am. Ceram. Soc., 79, 3033, 1996), and alumina (L. Bergstrom, "Rheological properties of Al_2O_3 and SiC-whisker composite suspensions", J. Mater. Sci., 31, 5257, 1996). Thickeners represent a different group of polymeric additives used for adjustment and control of the rheological properties. They are commonly used to increase the viscosity of the liquid to reduce the settling and thus prevent segregation. In WO 98/00257 it is shown that by the addition of suitable thickeners it is possible to prevent settling of cemented carbide slurries while still producing suitable rheological characteristics for spray drying.

[0005] Polyelectrolytes are usually the dispersant of choice when preparing aqueous inorganic powder suspensions. The popularity of polyelectrolytes stems from their low cost and high efficiency in dispersing many different kinds of powders in aqueous media. The effect of polyelectrolyte addition on the colloidal stability and rheological behaviour is determined by a complex interplay between the polyelectrolyte, the powder surface and the solution phase. In order to understand the adsorption behaviour of polyeletrolytes and the nature of the induced interparticle forces, one has to consider the surface chemistry of the solid phase as well as the solution properties of the polyelectrolyte. Polyelectrolytes acquire a charge in aqueous solutions due to the dissociation of functional groups; i.e. both the conformation and charged fraction of the polyelectrolyte is strongly dependent on pH and ionic strength. The surface charge density of the solid phase is also controlled by the solution conditions. Fundamentally, the surface charge density is dependent on the number density of surface groups, the pKa values of the surface reactions and the ionic strength of the solution.

[0006] Previous studies have shown that pH is a very important parameter in controlling polyelectrolyte adsorption. It is useful to distinguish between pH regimes where the particle surface and the polyelectrolyte carry net charges of either the same or opposite sign. If the segment-surface interaction is purely electrostatic, adsorption will only take place if the polyelectrolyte bears a net charge of opposite sign. This is the basis of the general rule that an acidic powder, which displays a negative surface charge over most of the pH-range, can be dispersed using a positively charged, cationic polyelectrolyte. Oppositely, a basic powder, which carries a positive charge over most of the pH-range, can be dispersed using a negatively charged, anionic polyelectrolyte.

[0007] For example, well-dispersed, highly concentrated alumina suspensions have been prepared by Novich et al using low amounts (0.5-2 wt%) of a polyacrylate polyelectrolyte (US 4,904,411). They used the same type of dispersant for dispersing steel powder and zirconia. Novich et al were also able to disperse acidic powders like silica using a cationic polyelectrolyte called CORCAT P-12 and P-600.

[0008] Although these principles have been most useful for finding suitable dispersants for simple ceramic systems, the situation rapidly becomes more complex

when the number of particulate constituents in a slurry is increased. When the suspension contains mixtures of acidic and basic powders it is usually necessary to resort to trial and error to find a suitable dispersant for a specific system.

[0009] Hard metals - mixtures of WC and Co together with additional particulate constituents - are commercially important systems which have to be dispersed and spray dried for subsequent mass production of, for example, inserts for metal cutting tools. However, the slightly soluble and widely different acid/base properties of the two main particulate constituents (WC or rather the surface oxide WO_3 is acidic and CoO is basic) make this system difficult to disperse in polar media. The current process technology typically involves dispersing the powders in an ethanol-rich medium under strong agitation prior to spray drying. The solids loading must be relatively low, around 20 vol%, to keep the viscosity at a sufficiently low level. With robust, well dispersed suspensions of WC+Co-based particulate mixtures there is a possibility to increase the solids content and thus reduce the energy consumption during spray drying. There is also a large interest in developing well dispersed aqueous suspensions of WC+Co-based particulate mixtures to eliminate the explosion hazards and reduce the environmental impact of ethanol-based suspensions.

Summary of the invention

[0010] The present invention provides a procedure for making well dispersed suspensions comprising mixtures of WC and Co powders displaying a low viscosity, which remain stable over an extended period of time. The invented aqueous and ethanolic slurries are suitable as the starting materials for all wet processing techniques for producing materials for these powders. These processing routes include spray drying to make spherical, free flowing granules of the fine powder.

[0011] The procedure involves mixing the powders, based on mixtures of WC and Co with additional constituents suitable for making cemented carbides, with water, ethanol or mixtures of ethanol and water, and a polyethylenimine-based dispersant to achieve a well-dispersed suspension suitable for spray drying.

[0012] According to a preferred embodiment the WC+Co-based slurries can be used to produce inserts for metal cutting tools.

Detailed description of the preferred embodiments

[0013] The present invention is directed to dispersing mixtures of WC and Co powders in aqueous and ethanolic media to produce well-dispersed slurries having a low viscosity. Further, the invention provides a method for making homogeneous powder bodies by different types of wet processing techniques, including spray drying and subsequent dry pressing. The invention provides a method for processing cemented carbide powders in aqueous and ethanolic media for production of inserts for metal cutting tools.

[0014] More specifically, the procedure according to the invention comprises forming a slurry including the powders, a polyethylenimine-based dispersant for the solid phases and water or ethanol or mixtures of water and ethanol as the medium. The resulting slurry should be well-dispersed, robust and display a low viscosity to facilitate subsequent wet processing, e.g. spray drying.

[0015] By a low viscosity, we mean that a 20 vol% slurry should display a viscosity of less than 30 mPas at a shear rate of 100 l/s, preferably less than 15 mPas at this shear rate and less than 1000 mPas at a shear rate of 100 l/s for a 40 vol% slurry.

[0016] By a robust slurry, we mean that its rheological properties should be stable over an extended period of time. For a 20 vol% slurry, the viscosity should increase less than 20 % over a period of 24 hours.

[0017] The invention is directed to all kinds of WC+Co-based powder slurries intended for manufacturing of cemented carbides. This includes additions of carbides and nitrides of titanium, tantalum, hafnium and/or niobium to the WC+Co mixture. It is particularly suited for fine, sub-micron-sized, particles but also applicable to coarser particles. The dispersion medium can be ethanol, water or mixtures of ethanol and water. While it is preferable to use distilled or deionized water for producing aqueous slurries, ordinary tap water is also suitable. The dispersants that are able to produce well-dispersed WC+Co-based slurries are polyelectrolytes, more specifically a cationic polyelectrolyte of the polyethylenimine type. The polyethylenimine type dispersants consist of a general backbone based on the monomer $(CH_2CH_2NH)_x$ and contain both primary, secondary and tertiary amine groups. An important property is that the polyethylenimine-based dispersant is able to disperse the WC+Co-based powder mixture at the inherent pH of the slurry; hence, no addition of acid or base is needed.

[0018] The powder, the dispersant and the polar dispersion medium may be combined in any suitable manner. In a preferred embodiment, the slurry is made by mixing the dispersant with ethanol, water or mixtures thereof and then adding the powders to the solutions. Generally, the amount of dispersant used in the mixture is 0.1-10 wt%, preferably 0.1-1 wt%. The solids loading is 10-50 vol%, preferably 20-40 vol%, which is the most suitable range for spray drying. All of the components are mixed in a high-energy mixer, e.g. a ball mill or a planetary mill. Mixing proceeds for a period from 10 minutes to 48 hours; 30 minutes to 2 hours are preferred mixing times in a planetary mill for solids loadings between 20 and 40 vol%.

[0019] The present invention also relates to a method of making cemented carbide or cermets bodies by powder metallurgical methods including wet milling in water and/or ethanol of powder forming hard constituents and binder phase and pressing agent to form a slurry, drying

the slurry to form a powder by spray drying, pressing the powder to form bodies of desired shape and dimension and finally sintering. The method is characterised in adding to the slurry as dispersant 0.1-10 wt%, preferably 0.1-1 wt%, of a polyethylenimine-based polyelectrolyte. Most preferably, the average molecular weight of the polyethylenimine-based polyelectrolyte is in the range 5000 to 50000, preferably 10000 to 30000.

[0020] The invention has been described with reference to WC-Co-based cemented carbides. It is obvious the invention can be applied also to the manufacture of hard materials based on carbides and nitrides of Ti, Ta, Hf and/or Nb and Co and/or Ni often referred to as cermets.

Example 1

[0021] An aqueous slurry at 20 vol% solids loading of a mixture of WC and Co powders (92 wt% WC and 8 wt% Co) displaying a low viscosity was prepared in the following manner. 355 grams of a WC+Co powder with an average particle size of 1.2 µm were mixed with 1.07 grams (0.3 wt%) of polyethylenimine with an average molecular weight of 10,000 from Polysciences Inc and 96 grams of water. The components were mixed together in a planetary mill for a total mixing time of 30 minutes divided into three 10-minute periods. The resulting slurry displayed a low viscosity of 9 mPas at a shear rate of 100 l/s and 90 mPas at a shear rate of 1 l/s.

Example 2

[0022] An aqueous slurry at 20 vol% solids loading of a mixture of WC and Co powders (92 wt% WC and 8 wt% Co) displaying a low viscosity was prepared in the following manner. 355 grams of a WC+Co powder with an average particle size of 1.2 µm were mixed with 3.55 grams (1 wt%) of polyethylenimine with an average molecular weight of 25,000 from Aldrich Chemicals and 96 grams of water. The components were mixed together in a planetary mill for a total mixing time of 30 minutes divided into three 10-minute periods. The resulting slurry displayed a low a viscosity after 12 hours of subsequent stirring; it was 8 mPas at a shear rate of 100 l/s and 15 mPas at a shear rate of 10 l/s. Ageing the slurry for an additional 24 hours under continuous stirring increased the viscosity marginally; it was 9 mPas at a shear rate of 100 l/s and 18 mPas at a shear rate of 10 l/s.

Example 3

[0023] An aqueous slurry at 40 vol% solids loading of a mixture of WC and Co powders (92 wt% WC and 8 wt% Co) displaying a low viscosity was prepared in the following manner. 414 grams of a WC+Co powder with an average particle size of 1.2 µm were mixed with 1.24 grams (0.3 wt%) of polyethylenimine with an average molecular weight of 10,000 from Polysciences Inc and 42 grams of water. The components were mixed together in a planetary mill for a total mixing time of 30 minutes divided into six 5-minute periods. The resulting slurry displayed a relatively low viscosity; it was 450 mPas at a shear rate of 100 l/s.

Example 4

[0024] A slurry at 20 vol% solids loading of a mixture of WC and Co powders (92 wt% WC and 8 wt% Co) in an ethanol/water mixture (80% ethanol) displaying a low viscosity was prepared in the following manner. 355 grams of a WC+Co powder with an average particle size of 1.2 µm were mixed with 3.55 grams (1 wt%) of polyethylenimine with an average molecular weight of 25,000 from Aldrich Chemicals and 61 grams of ethanol and 15 grams of water. The components were mixed together in a planetary mill for a total mixing time of 30 minutes divided into three 10-minute periods. The resulting slurry displayed a low viscosity after 12 hours of subsequent stirring; it was 13 mPas at a shear rate of 100 l/s and 25 mPas at a shear rate of 10 l/s.

Example 5

[0025] An ethanol-based slurry at 20 vol% solids loading of a mixture of WC and Co powders (92 wt% WC and 8 wt% Co) displaying a low viscosity was prepared in the following manner. 355 grams of a WC+Co powder with an average particle size of 1.2 µm were mixed with 1.78 grams (0.5 wt%) of polyethylenimine with an average molecular weight of 25,000 from Aldrich Chemicals and 76 grams of ethanol. The components were mixed together in a planetary mill for a total mixing time of 75 minutes divided into five 15-minute periods. The resulting slurry displayed a low a viscosity after 12 hours of subsequent stirring; it was 26 mPas at a shear rate of 100 l/s and 50 mPas at a shear rate of 10 l/s.

Example 6 (prior art)

[0026] As an example of prior art, an aqueous slurry at 20 vol% solids loading of a mixture of WC and Co powders (92 wt% WC and 8 wt% Co) and polyethylene glycol (PEG) as dispersant was prepared in the following manner. 355 grams of a WC+Co powder with an average particle size of 1.2 µm were mixed with 7.1 grams (2 wt%) of polyethylene glycol with an average molecular weight of 3,400 and 96 grams of water. The components were mixed together in a planetary mill for a total mixing time of 30 minutes divided into three 10-minute periods. The resulting slurry was flocculated and displayed a relatively high viscosity; it was 50 mPas at a shear rate of 100 l/s and 4000 mPas at a shear rate of 1 l/s.

Example 7

[0027] An ethanol-based slurry at 20 vol% solids loading of a mixture of WC, TaC, TiC, TiN and Co powders (20 wt% WC, 20 wt% TaC, 25 wt% TiC, 20 wt% TiN and 15 wt% Co) displaying a low viscosity was prepared in the following manner. 1000 grams of WC+TaC+TiC+TiN+Co powder with an average particle size of 1.3 μm were mixed with 3.00 grams (0.3 wt%) of polyethylenimine with an average molecular weight of 25,000 from Aldrich Chemicals and 421 grams of ethanol/water (90 wt% ethanol and 10 wt% water) and 35 grams of polyethyleneglycol with an average molecular weight of 3,500 from BASF. The components were mixed together in a ball mill for a total mixing time of 100 h. The resulting slurry displayed a low viscosity of 25 mPas at a shear rate of 100 l/s.

Example 8

[0028] An water-based slurry at 20 vol% solids loading of a mixture of WC, TaC, TiC, TiN and Co powders (20 wt% WC, 20 wt% TaC, 25 wt% TiC, 20 wt% TiN and 15 wt% Co) displaying a low viscosity was prepared in the following manner. 1000 grams of WC+TaC+TiC+TiN+Co powder with an average particle size of 1.3 μm were mixed with 3.00 grams (0.3 wt%) of polyethylenimine with an average molecular weight of 25,000 from Aldrich Chemicals and 514 grams of water and 35 grams of polyethyleneglycol with an average molecular weight of 3,500 from BASF. The components were mixed together in a ball mill for a total mixing time of 100 h. The resulting slurry displayed a low viscosity of 30 mPas at a shear rate of 100 l/s.

Example 9

[0029] An ethanol-based slurry at 20 vol% solids loading of a mixture of WC, TaC, TiC, TiN and Co powders (87 wt% WC, 3 wt% TaC, 2 wt% NbC, 2 wt% TiC, 0.5 wt% TiN and 5.5 wt% Co) displaying a low viscosity was prepared in the following manner. 1000 grams of WC+TaC+TiC+TiN+Co powder with an average particle size of 6.0 μm were mixed with 5.00 grams (0.5 wt%) of polyethylenimine with an average molecular weight of 25,000 from Aldrich Chemicals and 230 grams of ethanol/water (90 wt% ethanol and 10 wt% water) and 20 grams of polyethyleneglycol with an average molecular weight of 3,500 from BASF. The components were mixed together in a ball mill for a total mixing time of 100 h. The resulting slurry displayed a low viscosity of 29 mPas at a shear rate of 100 l/s.

Example 10

[0030] An ethanol-based slurry at 20 vol% solids loading of a mixture of WC, TaC, TiC, TiN and Co powders (84 wt% WC, 4 wt% TaC, 2 wt% NbC, 3 wt% TiC, 0.5 wt% TiN and 6.5 wt% Co) displaying a low viscosity was prepared in the following manner. 1000 grams of WC+TaC+TiC+TiN+Co powder with an average particle size of 6.0 μm were mixed with 5.00 grams (0.5 wt%) of polyethylenimine with an average molecular weight of 25,000 from Aldrich Chemicals and 235 grams of ethanol/water (90 wt% ethanol and 10 wt% water) and 20 grams of polyethyleneglycol with an average molecular weight of 3,500 from BASF. The components were mixed together in a ball mill for a total mixing time of 100 h. The resulting slurry displayed a low viscosity of 30 mPas at a shear rate of 100 l/s.

Claims

1. A well dispersed aqueous or ethanolic slurry with low viscosity for spray drying with a solids loading 10-50 vol% intended for manufacturing of cemented carbide or cermets bodies
characterised in containing as dispersant 0.1-10 wt% of a polyethylenimine-based polyelectrolyte.

2. A slurry according to claim 1 **characterised in** containing as dispersant 0.1-1 wt% of a polyethylenimine-based polyelectrolyte.

3. A slurry according to any of claims 1 or 2, **characterised in that** the average molecular weight of the polyethylenimine-based polyelectrolyte is in the range 5000 to 50000, preferably 10000 to 30000.

4. Method of making cemented carbide or cermets bodies by powder metallurgical methods including wet milling in water and/or ethanol of powder forming hard constituents and binder phase and pressing agent to form a slurry, drying the slurry to form a powder by spray drying, pressing the powder to form bodies of desired shape and dimension and finally sintering **characterised in** adding to the slurry as dispersant 0.1-10 wt% of a polyethylenimine-based polyelectrolyte.

5. Method according to claim 4 **characterised in** adding as dispersant 0.1-1 wt% of a polyethylenimine-based polyelectrolyte.

6. A slurry according to any of claims 4 or 5, **characterised in that** the average molecular weight of the polyethylenimine-based polyelectrolyte is in the range 5000 to 50000, preferably 10000 to 30000.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 11 0490

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A,D	US 4 904 411 A (NOVICH BRUCE E ET AL) 27 February 1990 (1990-02-27) * claims 1,5,7 *	1	B01F17/00
A	US 5 047 181 A (OCCHIONERO MARK A ET AL) 10 September 1991 (1991-09-10) * column 4, line 62 - column 6, line 57 *	1	
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 124 (C-416), 17 April 1987 (1987-04-17) & JP 61 263627 A (DAI ICHI KOGYO SEIYAKU CO LTD), 21 November 1986 (1986-11-21) * abstract *	1	
A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 297 (C-519), 12 August 1988 (1988-08-12) & JP 63 065940 A (NIPPON SHOKUBAI KAGAKU KOGYO CO LTD), 24 March 1988 (1988-03-24) * abstract *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)
B01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	3 September 2001	Clement, J-P

CATEGORY OF CITED DOCUMENTS

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